RAMAN SCATTERING IN CRYSTALLINE SOLIDS

DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE OF

Master of Philosophy

IN

PHYSICS

BY

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ACKNOWLEDGEMENTS

It is a pleasure to express my deepest sense of gratitude and indebtedness to my Supervisor Dr. J.P. Srivastava, for his keen interest, constant guidance, invaluable suggestions and encouragement during the course of work.

I am thankful to Prof. Israr Ahmad, Chairman, Department of Physics, A.M.U., Aligarh for providing the working facilities in the Department and taking interest in the progress of this work.

I am indebted to Prof. M.Z.R. Khan for his role in providing me the opportunity of pursuing higher studies and for the constant encouragement.

I gratefully thank Prof. H.D. Bist, Department of Physics, I.I.T., Kanpur for allowing me to make use of facilities in his laboratory. His constant help and suggestions have inspired me to take up my investigations with a fresh zeal.

I am very thankful to Dr. Mushtaq Ahmad, Lecturer, Department of Physics, AMU, for his constant help, encouragement and suggestions. My special thanks are due to Mr. P.K. Khulbe, Laser Raman Spectroscopy Lab, I.I.T.,

Kanpur, for his help in recording the Raman spectra. My thanks are also due to Mr. P.S.R. Prasad and Mr. S.S. Sathaiah of the same laboratory, for their helpful discussions and cooperation.

I feel sincerely indebted to all of my Bangladeshi friends, specially M/S. Nazma Akhter Banu, Md. Hafizur Rahman, Md. Ekram Ali Shaik and Nimai Chan Biswas for their encouragement and help during my work. I am also thankful to Mr. Mohd. Rashid, for typing this dissertation carefully.

The technical assistance from the staff of the Department of Physics, AMU, is appreciated. Financial support from the Govt. of India and DSA/COSIST, AMU, are gratefully acknowledged.

Finally, I would like to take this occasion to thank my parents, parents-in-law, my wife, brothers and brothers-in-law for their tremendous patience and encouragement.

M. Abul Hossain

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GENERAL INTRODUCTION

Structural phase transitions in crystals between higher symmetry and lower symmetry phases have attracted the attention of both experimentalists and theoreticians [1]. Raman, infrared and other vibrational spectroscopic studies provide deeper insight into the microscopic origin of structural phase transitions. In the Raman technique, the light is scattered due to the fluctuations in the dielectric tensor of a material. Fluctuations of certain physical quantities are coupled to the fluctuations in the dielectric tensor; near the transition the fluctuations of some of these quantities are enhanced. This makes the Raman scattering an important tool for the study of structural phase transitions, particularly orientational order-disorder type of transitions [2].

There have been many investigations of structural phase transitions in perovskite-type ABX_3 compounds where the structure consists of BX_6 octrahedra forming a three dimensional network. Perovskite-type layer structures of general formula $(C_nH_{2n+1}NH_3)\ MCl_4$ consist of layers of corner sharing MCl_6 octrahedra with alkylammonium chains occupying the A sites. Several phase transitions in these compounds are very well understood.

For short chain compounds these transitions are connected with the disordering of the alkylammonium groups - which move on the surface of a cone the axis of which is perpendicular to the layer axis and a deformation on the MCl_4 layers. In contrast very little is known about the structure and possible structural phase transitions in alkylammonium mercuric chloride family of compounds.

Further, the study of vibrational properties help in understanding the dynamics of orientation of molecular groups and atoms in crystals. Vibrational properties also provide information about molecular structure and the nature of forces that bind the various atomic and molecular units inside a crystal. The Raman scattering and infrared absorption spectroscopic measurements are being used to study the vibrational properties. These spectroscopic techniques provide the means of studying the effect of crystalline field on vibrations of the crystals through polarization measurements. The advantage of Raman scattering measurements over the absorption spectroscopy is that the entire vibrational spectrum can be scanned in a single run of the spectrum whereas latter requires separate measurements for far-infrared (FIR) and near-infrared (NIR) spectral region.

The present work includes the study of the structural phase transition and vibrational assignment of

Methylammonium mercury chloride $(CH_3NH_3)HgCl_3$.

Chapter I describes the group theoretical methods for the classification of normal modes, anharmonicity and interaction of vibration, theory of infrared and Raman scattering and their selection rules. In addition, a detailed review of the various kinds of structural phase transitions has been given in this chapter.

In Chapter II, we have discussed the details on crystal growing, verification of crystal structure alongwith a brief description of the principle of working of equipments used for our studies.

Chapter III describes our experimental observations i.e., the vibrational analysis of spectra and the characteristics of the observed structural phase transition (STP). The phase transition is characterized with the temperature dependence of ν_5^{C-N} (A_1) stretching mode which appears the most thermosensitive. The sharp changes and discontinuities observed in frequency shift and FWHM alongwith a discontinuous change in intensity with temperature at 57°C are typical features associated with phase transitions of the first order type. Broadening of the band at higher temperature suggests the appreciable motion of the $CH_3NH_3^+$ group during phase transition.

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CHAPTER - I

THEORETICAL BACKGROUND

THEORETICAL BACKGROUND

1.1 INTRODUCTION

Since long IR and Raman spectroscopy has been playing an important role in solving chemical problems such as molecular structure, molecular interactions, hydrogen bonding, absorption, phase transition and related phenomena [1,2]. A number of vibrational spectroscopic studies have been performed on the crystalline materials. Their IR and Raman spectra provide information about freqencies, band width and relative intensities of the different modes of vibration of the molecular systems present and that of the lattice which can be used to investigate the structure of molecular species, nature of the crystalline forces as well as structure and symmetry of the crystal itself. With the invention of laser, the Raman scattering technique has become powerful tool as IR absorption for the analysis and identification of materials and for the study of molecular and lattice dynamics and molecular structure as well as structural phase change [3]. Extensive information about the structure and symmetry of molecules as well as their vibrational energies can be obtained from these spectra. This chapter is intended as an introduction to the principles and practice of those aspects of Raman and IR spectroscopy which are of major interest in our present work.

1.2 DYNAMICS OF A CRYSTAL

A crystal can be regarded as a mechanical system of nN paricles where n and N are total number of unit cells and number of particles per unit cell in the crystal respectively. There will be 3nN degrees of freedom for such a system. These may be classified as 3 translations and (3nN-3) linearly independent normal modes of oscillation of the crystal [4]. Frequencies of vibrational modes occur as 3N roots of the secular equations involving the wave vector which may take n values. Three of these roots approach zero as the wave vector tends to zero and constitute acoustic branches. The remaining (3N-3) branches are termed optical branches and approach finite limit as the wave vector tends to zero and constitute acoustic branches. These constitute the fundamental spectra of the crystal. The optical phonon modes are divided into internal and external modes of vibration. In case the molecule vibrates as a whole, the molecular groups performed rigid body motion. Such vibrations are known as external vibrations or lattice vibrations and are separated into two types. Translational modes involve the translation of the molecular groups in the crystal whereas rotational or librational modes involve quasi-rotation of molecular groups about their centre of

gravity and therefore require the presence of polyatomic groups in the crystals [5]. The atoms that comprise a molecular group vibrate within the molecular group. Such vibrations involving non-rigid molecular motions and allowing for the coupling between different groups and crystal periodicity are known as internal vibrations.

All these vibrations are governed by inter and intramolecular interactions and may be described interms of a simple modes of motion known as normal modes.

A normal mode has the following properties [6,7]:
(a) Each atom of the system oscillates about its equilibrium position with a simple harmonic motion having the same frequency and phase.
(b) The relative velocity and amplitude of an individual atom depend on its mass and the nature of motion is so governed that no resultant translation or rotation of the system as a whole takes place.

When a group of atoms constituting an ion or molecule goes to build up a crystal its normal modes usually undergo three types of modifications : (i) splitting of the degenerate vibrations, (ii) increase in multiplicity due to the unit cell containing more than one molecule, and (iii) alternations in the selection rules. The vibrational potential energy (V) associated with a unit cell under

harmonic approximation can be expressed as [8,9]

$$V=\sum_j (V_j^o + V_j^{'}) + \sum\sum_{jk} V_{jk}+V_L+ \sum_j V_{Lj} \quad \ldots\ldots (1.1)$$

Where the summations extended over all the molecular units in the unit cell. The terms used above represent as follows :

V_j^o - the potential energy function of the free j^{th} molecule.

$V_j^{'}$ - the perturbation of V_j^o due to the equilibrium field of the crystal at the site of the j^{th} molecule. It can cause shifts in fundamental frequencies and changes in selection rules.

V_jK - represents the terms involving displacement coordinates in the J^{th} and K^{th} molecules.

V_l - represents the terms involving the relative displacement and rotational orientation of molecules with respect to each other, and thus represents the lattice potential.

V_{lj} - contains terms involving interaction between the lattice coordinates and internal coordinates.

1.3 CLASSIFICATION OF PHONONS

Because of intermolecular interactions, the symmetry of a molecule is generally lower in the crystalline state than in the gaseous (isolated) state.

This lowering in symmetry may split the degenerate vibrations and activate infrared or Raman inactive vibrations. In addition, the spectra obtained in the crystalline state exhibit vibrations due to the translatory and rotatory motions of a molecule in the crystalline lattice. For the analysis of the vibrational spectra and the classification of phonons in crystals, two group theoretical methods are generally used :

(a) Unit cell approach [10]

(b) Site symmetry approximation [11]

The application of these methods has been illustrated by several authors [12,13,14]. Fateley et al. [15] have suggested some practical rules for classification of phonons using site symmetry approach. A brief review of the two methods is given here. Both the methods, however, give same results [16].

1.3.1 Unit Cell Approach

A crystal containing n unit cells of N-atoms each will have 3nN modes of vibration. In the unit cell approach, it is assumed that atoms or molecules at the equivalent lattice positions are in the same state of motion with no phase difference. In this approach only 3N modes of unit cell can serve the purpose of describing the dynamics

of the whole crystal and hence the approach consists in finding the total character representation for the unit cell using the following formula [17],

$$\chi(N) = N^R (\pm 1 + 2 \cos \phi_R) \quad .... \quad 1.2$$

where N^R is the number of atoms remaining invarient under the operation R. The operation R is defined by an angle ϕ_R; +1 and -1 are accounted respectively for proper and improper rotations. The characters for acoustic translation vibrations $\chi(ta)$, optical translatory modes $\chi(to)$ and libratory modes $\chi(l)$ are determined by using the following formulae :

$$\chi(ta) = (\pm 1 + 2 \cos \phi_R) \qquad (1.3)$$

$$\chi(to) = N^R(s)(\pm 1 + 2 \cos \phi_R) \qquad (1.4)$$

$$\chi(l) = N^R(p)(1 \pm 2 \cos \phi_R) \qquad (1.5)$$

where $N^R(s)$ is the number of structural groups that remain invariant under a symmetry operation R and $N^R(p)$ is the number of polyatomic groups that remain invariant under a symmetry operation R.

The number of modes belonging to a particular species of an irreducible representation can be obtained by reducing the representation Γ, using following relation [18]

$$n^k = \frac{1}{g} \sum_i h_i \chi_i (R) \chi_i^k (R) \qquad (1.6)$$

where n^k is the number of times an irreducible representation of the species k appears in the reducible representation Γ, χ_i^k (R) and χ_i (R) are the characters of i^{th} class of operations describing irreducible and reducible representations respectively. g is the order of the group and h_i is the number of group operations in the i^{th} class of the irreducible representation χ_i^k. The normal modes are classified by making specific selections of the representation Γ and its appropriate character $\chi_i(R)$.

The number of internal modes of vibration can be calculated by substracting the number of external modes (translatory + rotatory) from the total number of modes

$$\chi(n_i) = \chi_i(N) - [\chi_i(to) + \chi_i(l)] \qquad (1.7)$$

1.3.2 Site symmetry approximation - Correlation method

Halford [11] assumed that only the local potentials are mainly responsible for the dynamics of mono-and polyatomic groups in crystals. Therefore, he classified the normal modes into the species of local symmetry point group, also termed as site group, by correlating the symmetry species of the point group of free molecular ion to those of the site group and thus he neglected the interaction between the different groups in the same unit cell. The site group characterizes the symmetry of the crystalline field around

the site. Thus the geometrical structure of a molecule or ion occupying the given site is determined by the symmetry of that site. A molecule may exhibit lower symmetry in the crystal than in gas phase, because in the crystalline solid it must conform to the symmetry of its site. Therefore, the site group is necessarily a subgroup of the unit cell or factor group which describes the symmetry of the free molecules. The correlation chart can be set up between various site groups and factor groups, identified for each equivalent set of atoms. These species of the site group for the translations and rotations are then correlated with species of factor group. This correlation explicitly identifies the species of lattice vibrations in the crystal and further allows prediction of infrared and Raman activity. The total reducible representation for lattice vibrations is obtained by the summation of reducible representation for each equivalent set of atoms or ions in the crystals.

Before applying the correlations of site to factor group following terms have been defined by Fateley et al. [15]

1. t^{ν}, R^{ν} - are defined as the number of translations and rotations respectively in a site species. This number can take the value of zero, one, two or three depending on whether none, one, two or three translations or rotations are contained in the site species, respectively. These numbers are obtained from the character table.

2. f^{γ}, f_R^{γ} - as degrees of freedom for translations and rotations respectively of a site species γ. These can be calculated from the relations.

$$f^{\gamma} = nt^{\gamma} \quad \ldots\ (1.8)$$

$$f_R^{\gamma} = nR^{\gamma} \quad \ldots\ (1.9)$$

where n is the number of atoms/ions/molecules in an equivalent set.

3. a_γ represents the degrees of freedom contributed by each site species γ to a factor group species α. The values of a_γ can be calculated as follows :

$$f^{\gamma} = a_\gamma \sum_\alpha C_\alpha^{\gamma} \quad \ldots\ (1.10)$$

$$f_R^{\gamma} = a_\gamma \sum_\alpha C_\alpha^{\gamma}$$

4. C_α - is the degeneracy of the species α of the factor group.

The reducible representation for internal vibrations of a molecular group is obtained by using the free state symmetry of that group. These symmetry species for free state symmetry group are then correlated with the site symmetry species. Further correlation of site symmetry species with the factor group species yeilds the reducible representation for internal vibrations specifying the infrared and Raman activity of the different internal vibrations.

The total representation for internal modes is then added to the representation for lattice vibrations to get the reducible representation for total normal modes of vibrations of the crystal.

1.4 INTERNAL MODES OF VIBRATION OF MOLECULAR GROUPS OF THE CRYSTALS UNDER STUDY

The atoms those comprise a molecular group vibrate within the molecular group. Such vibrations involving non rigid molecular motions are known as internal vibrations. The internal modes of vibration of the molecular groups present in the crystals under study have been discussed here. The molecular groups present in the crystals are $HgCl_3^-$ and $CH_3NH_3^+$. The first one is XY_3 type molecules having planar D_{3h} symmetry and the second group belongs to ZXY_3 type molecules with C_{3v} symmetry. The symmetries described here correspond to the free states of molecular groups.

1.4.1 Modes of vibration of $HgCl_3^-$ ion

The internal vibrations of $HgCl_3^-$ are classified into A_1' , A_2'' and E" species according to D_{3h} symmetry. Its symmetry is taken D_{3h} treating it as XY_3 type molecule. Six normal modes of vibration are distributed as $A_1' + A_2'' + E''$. The symmetric A_1' stretching mode denoted as ν_1 is Raman active but infrared inactive. The asymmetric A_2'' mode denoted

Table 1.1 : Classification of different modes of ($HgCl_3$) group under D_{3h} (XY_3 type) symmetry.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	n	t	R	Internal modes		Activity	
										n_i	Designation	IR	Raman
A_1	1	1	1	1	1	1	1	-	-	1	ν_1	f	P(XX + YY, ZZ)
A_2	1	1	-1	1	1	-1	1	-	1	-		$f(R_z)$	f
E	2	-1	0	2	-1	0	1	1	-	-		$P(T_x,T_y)$	P(XX - YY,XY)
A_1	1	1	1	-1	-1	-1	-	-	-	-	-	f	f
A_2''	1	1	-1	-1	-1	1	2	1	-	1	ν_2	$P(T_z)$	f
E"	2	-1	0	-2	1	0	3	-	1	2	ν_3, ν_4	$f(R_x,R_y)$	P(XZ, YZ)

n - Total number of modes

t - Translational modes

l - Libratory modes

n_i - Internal modes.

as ν_2 is Raman forbidden but infrared active. The two doubly degenerate modes E" denoted as ν_1 and $\nu 2$ are Raman active only. The distribution of the modes among the species of free ion symmetry group is shown in table 1.1.

1.4.2 Modes of Vibration of $CH_3NH_3^+$ ion

The internal vibrations of $CH_3NH_3^+$ are classified into A_1, A_2 and E species according to C_{3v} symmetry. Its symmetry is taken C_{3v} treating it as ZXY_3 type molecule where Z represents CH_3 group and XY_3 is used for NH_3. Eighteen normal modes of vibration are distributed as $5A_1$ + A_2 + 6E. The five non degenerate A_1 type modes are denoted as $\nu_1, \nu_2, \nu_3, \nu_4$ and ν_5 and one non-degenerate A_2 type is denoted as ν_6. The mode ν_7 to ν_{12} represent six doubly degenerate E type modes. The A_1 and E type modes are active in infrared and Raman spectra whereas the A_2 type mode is infrared-Raman inactive. The distribution on the modes among the species of free ion symmetry group is shown in table 1.2.

1.5 ANHARMONICITY AND INTERACTION OF VIBRATION

The effect of anharmonicity may be evidenced by the appearance of combinations or overtones in the vibrational spectra arising from simultaneous changes of state by two or more quanta of vibrational energy. Such modes in crystalline solids are explained on the basis of multiphonon processes[19

Anharmonicity normally affects the molecular vibrations in two ways [20,21].

Table 1.2 : Classification of different modes of (CH_3NH_3) group under C_{3v} (ZXY_3 type) Symmetry.

C_{3v}	E	$2C_3$	$\sigma 3_v$	n	t	l	Internal modes		Activity	
							n_i	Designation	IR	Raman
A_1	1	1	1	6	1	0	5	$\nu_1, \nu_2, \nu_3, \nu_4, \nu_5$	$P(T_Z)$	P(XX+YY,ZZ)
A_2	1	1	-1	2	0	1	1	ν_6	$f(R_Z)$	f
E	2	-1	0	8	1	1	6	$\nu_7, \nu_8, \nu_9, \nu_{10}, \nu_{11}, \nu_{12}$.	$P(T_X,T_Y)$; (R_X,R_Y)	P(YX-YY,XY,YZ, ZX)

n - Total number of modes

t - Translatory modes

l - Libratory modes

n_i - Internal modes.

Firstly, the selection rule, derived for the harmonic oscillator, $\Delta v = \pm 1$ (v denotes the vibrational quantum) ceases to be rigorous and transitions with $\Delta v = \pm 1, \pm 2, \pm 3$ .... become allowed. Secondly, the vibrational energy levels are not spaced apart equally by the quantity $h\nu$ and combination bands are also allowed. The intensity of the overtone or combination bands is directly related to the anharmonic character of vibrations. If overtone or combination bands are not observed the harmonic approximation works excellent. Observation of strong overtone or combination bands indicate the presence of anharmonic.

Anharmonicity can be of two types [22,23] : Mechanical and electrical.

The mechanical anharmonicity is associated with the deviation of the potential function for a given mode from the harmonic form. Normal vibrations rest on the assumption that in the ranges of amplitude of oscillations involved the quadratic terms in the potential energy plays the dominant role in the motion. But in actual vibrations the cubic, quartic and higher terms in the potential energy may be appreciable to make the oscillations anharmonic. The potential energy function for a particular vibration is written as

$$V = \frac{1}{2}k_2Q^2 + K_3Q^3 + K_4Q^4 + \ldots \qquad \ldots \quad (1.11)$$

where Q is the normal coordinate and K_i is the force constant.

Electrical anharmonicity depends on the quadratic and higher terms in the expression of the instantaneous dipole moment given by

$$\mu = \mu_0 + \mu_1 Q + \mu_2 Q^2 + \ldots \qquad \ldots \qquad (1.12)$$

In some cases the mechanical vibration is harmonic (K_3, K_4 ... = zero), but the change is related to vibrations through the well known equation [23],

$$G(V) = (V + \tfrac{1}{2})\, we - (V + \tfrac{1}{2})^2\, We\, Xe + \ldots \qquad (1.13)$$

where G(1) - G(o), G(2) - G(o) etc give the observed band frequencies ν, 2ν etc. Conversely, the observed values of ν and 2ν [not the same as $2(\nu)$] lead to We, WeXe [20] and cubic potential constant [22]. Also the relative intensities of ν and 2ν bands lead to μ_2/μ_1 [23].

The relations are ;

$$We\, Xe = \frac{2(\nu) - 2\nu}{2} \qquad \ldots \qquad (1.14)$$

$$We = \nu + 2WeXe$$

$$k_3 = \pm \left[\frac{4}{15}\, We \mid WeXe \mid\right]^{\frac{1}{2}} \qquad \ldots \qquad (1.15)$$

$$\frac{\mu_2}{\mu_1} = \frac{-(K_3/We) \pm [I_{2\nu}/I_{\nu}\, 2\nu]^{\frac{1}{2}}}{1 \pm 5\, (K_3/We)[I_{2\nu}/I_{\nu}\, 2\nu]^{\frac{1}{2}}} \qquad \ldots \qquad (1.16)$$

where + sign in the last two equations refers to a negative value of WeXe and vice versa.

1.6 INFRARED ABSORPTION

1.6.1 General

The infrared absorption involves the interaction of IR radiation with matter. To a first approximation, it occurs through the changes in the electric dipole moment ($\vec{\mu}$) of the molecular unit arising due to its excitation to a higher vibrational level [24]. As vibrational frequencies of the molecular units match the energy of IR photon, enough information about the dynamics of these systems can be collected from the IR absorption data.

Coblentz [25] was among the first who made a systematic study of IR absorption in 1905. Since then a number of theoretical and experimental studies have been made on the subject.

1.6.2 Selection rules

According to quantum mechanics [24] the selection rules for the infrared spectra are determined by the transition modent integral.

$$[\vec{\mu}]_{ij} = \int \Psi_i(Q_a)\, \vec{\mu}\, \Psi_j(Q_a) dQ_a \quad .... \quad (1.17)$$

where $\vec{\mu}$ is the electric dipole moments in the electronic ground state and Ψ_i and Ψ_j are the vibrational eigen functions of the ground and excited states respectively. The activity of the normal vibration whose normal coordinate is Q_a, is being determined. By resolving the dipole moment into three components in the x,y and z directions, we obtain the following results :

$$[\vec{\mu}_x]_{ij} = \int \Psi_i(Q_a)\, \vec{\mu}_x\, \Psi_j(Q_a) dQ_a$$

$$[\vec{\mu}_y]_{ij} = \int \Psi_i(Q_a)\, \vec{\mu}_y\, \Psi_j(Q_a) dQ_a \quad .... \quad (1.18)$$

$$[\vec{u}_z]_{ij} = \int \Psi_i(Q_a)\, \vec{\mu}_z\, \Psi_j(Q_a) dQ_a$$

If one of these integrals is not zero, the normal vibration associated with the normal coordinate Q_a is IR active. If all the integrals are zero, the vibration is IR inactive. Since wave function Ψ_i belongs to totally symmetric representation [26], the coordinate x,y, or z and Ψ_j must belong to the same representation in order that the representation of their direct product will contain the totally symmetric representation. The simple selection rule for infrared activity can be stated as "A fundamental will be infrared active if the normal mode which is excited belongs to the same representation as anyone or several of the Cartesian coordinates." The character tables show to

which representation the Cartesian coordinates belong and therefore infrared activity of a fundamental will be known.

1.7 RAMAN SCATTERING

1.7.1 General

Light scattering experiments have become important for several years for investigating the properties of matter. They stand along with neutron diffraction, X-ray diffraction, spin resonance and infrared reflectivity as one of the principal means for investigating phase transitions in crystals. The symmetry information available from polarized scattering helps in determining static lattice structure.

When monochromatic radiation of frequency ν incident on a system like dust-free, transparent gases and liquids, or optically perfect, transparent solids, most of it is transmitted without change, but, in addition, some scattering of the radiation occurs. If the frequency content of the scattered radiation is analysed, there will be observed not only the frequency ν associated with the incident radiation but also in general, pairs of new frequencies of the type $\nu' = \nu \pm \nu_i$. Here ν_i represents a frequency characteristic of the molecule are found to lie principally in the ranges associated with transitions

between rotational, vibrational, and electronic levels. The scattered radiation usually has polarization characteristics different from those of the incident radiation, and both the intensity and polarization of the scattered radiation depend on the direction of observation [27].

Such scattering of radiation with change of frequency (or wave number) is called Raman scattering, after the Indian scientist C.V. Raman [28] who, with K.S. Krishnan, first observed this phenomenon in liquids in 1928. The effect had been predicted on the theoretical grounds in 1923 by A. Smekal [29]. Very shortly after the paper of Raman and Krishnan was published, Landsberg and Mandelstam [30] in Russia reported the observation of light scattering with change of frequency in quartz; and Cabannes [31] and Rocard [32] in France confirmed the finding of Raman and Krishnan.

In the spectrum of the scattered radiation, the new wave numbers (frequencies) are termed Raman lines, or bands, and collectively are said to constitute a Raman spectrum. Raman bands at frequencies less than the incident frequency i.e., of the type $\nu_s = \nu - \nu_i$ are referred to as Stokes bands, and those at frequencies $\nu_{AS} = \nu + \nu_i$ greater than the incident frequency are referred to as anti-Stokes bands.

A partial quantum mechaical explanation for Raman scattering phenomenon is as follows [33]. Here the radiation is treated classically and is regarded as the sources of perturbation of the molecular system which is treated quantum mechanically. The transitions between energy levels of the molecular system take place with the emission or absorption of radiation, provided the transition moment associated with the initial and final molecular state is non-zero. The transition moment is defined by

$$P_{fi} = \langle \psi_f | P_o | \psi_i \rangle \qquad .... \qquad (1.19)$$

using Dirac bracket notation. Here ψ_i and ψ_f are the wave functions for the initial and final states, respectively, and P_o is the induced dipole moment operator of the system. The induced dipole moment is given by

$$\bar{P}_o = \alpha \bar{E}_o \qquad .... \qquad (1.20)$$

where α is the polarisability of the molecule and $\bar{E}_o$ is the the electric field.

Thus in quantum mechanical terms, if a transition from initial state ψi to a final state ψf is induced by incident radiation of circular frequency ω_o, the transition moment amplitude associated with this change is given by

$$[P_o]_{fi} = \langle \psi_f | \alpha | \psi_i \rangle \; E_o \qquad .... \qquad (1.21)$$

The wave functions ψ_i and ψ_f and the polarisability tensor α are functions of all the coordinates of the system and the integral is over the whole coordinate space.

In equation (1.19) electric field vector has not been included in space integral. Above equation is adequate for the calculation of transition moment amplitude of molecular systems whose dimensions are small compared to the wavelength of the incident radiation. In such case the electric field vector will remain sensibly constant over the molecule. In higher order approximations and for large molecules, the vibration of the electric field over the molecular system must be taken into account. Scattering which is of electric quadrupole and magnetic dipole origin arises from this higher order treatment.

Equation (1.20) implies that the magnitude of the components of $\bar{P}$ are related to the magnitude of the components $\bar{E}$ by the three linear equations as given below :

$$[P_{XO}] = [\alpha_{xx}]_{fi} E_{xo} + [\alpha_{xy}]_{fi} E_{xo} + [\alpha_{zx}]_{fi} E_{xo}$$

$$[P_{yo}]_{fi} = [\alpha_{yx}]_{fi} E_{yo} + [\alpha_{yy}]_{fi} E_{yo} + [\alpha_{yz}]_{fi} E_{yo}$$

$$[P_{zo}]_{fi} = [\alpha_{zx}]_{fi} E_{zo} + [\alpha_{zy}]_{fi} E_{z0} + [\alpha_{zz}]_{fi} E_{z0} \quad \ldots (1.2$$

where

$$[\alpha_{xx}]_{fi} = \langle \psi_i | \alpha_{xx} | \psi_i \rangle$$

$$[\alpha_{xy}]_{fi} = \langle \psi_f | \alpha_{xy} | \psi_i \rangle \qquad \ldots\ (1.23)$$

and so on. $[\alpha_{xx}]_{fi}$, $[\alpha_{xy}]_{fi}$, ... are termed matrix elements of the polarisability tensor components α_{xx}, α_{xy}, α_{zz} ... for the transition $f \longleftrightarrow i$.

1.7.2 Selection rules for Raman Scattering

According to quantum mechanics, the vibration is Raman active if one of the six components of the polarizability tensor $\vec{\alpha}$ changes during the vibration. This can be determined by transition moment integral for Raman scattering

$$[\alpha]_{fi} = \int \psi_f(Q_a) \alpha \psi_i(Q_a) dQ_a \qquad \ldots\ (1.24)$$

The Raman activity of the normal vibration whose normal coordinate is Q_a, is being determined. Since $\vec{\alpha}$ consists of six components $\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}, \alpha_{yz}$ and α_{zx}; the equation (1.24) can be resolved into six equations :

$$[\alpha_{xx}]_{fi} = \int \psi_f(Q_a) \alpha_{xx} \psi_i(Q_a) dQ_a$$

$$[\alpha_{yy}]_{fi} = \int \psi_f(Q_a) \alpha_{yy} \psi_i(Q_a) dQ_a \qquad \ldots\ (1.25)$$

$$[\alpha_{zz}]_{fi} = \int \psi_f(Q_a) \alpha_{zz} \psi_i(Q_a) dQ_a$$

and so on.

If one of these integrals is not zero, the normal vibration associated with the normal coordinate Q_a is Raman active. If all the integrals are zero, the corresponding vibration is Raman inactive. In these integrals $\vec{\alpha}$ is one of the quadratic functions of the Cartesian coordinates, viz, x^2, y^2, z^2, xz, xy, $x^2 - y^2$ etc.

1.8 PHASE TRANSITIONS

Phase transitions occur when a substance changes its structure as a result of the variation in temperature, pressure or any other parameter like an applied magnetic or electric field [34]. The corresponding change in atomic position may not amount to a change in overall symmetry of the crystal. Both microscopic and macroscopic properties of the system depend on these transitions. Their studies are of importance for various applications of materials, like use of ferroelectrics as Piezoelectric component and pyroelectric detectors, computer core storage in magnetized ferrite raigs, liquid crystal displays etc. [34-37]. Various experimental techniques such as X-ray diffraction, neutron diffraction, Hall Coefficient, heat capacity measurement, elastic constant, susceptibility measurement, Raman and infrared spectroscopic studies etc [38] have been used to investigate phase transitions. Raman scattering

studies of structural phase transitions have been reviewed by Flury [39], Scott [40], Steigmier [41] and Nakamure [42]. These are important because at least one component of the soft mode of a continuous structural phase transition is always Raman active below the transition temperature [35]. A further advance of Raman technique is that it can provide information about the specific molecular motions involved in triggering the phase transition [43].

1.8.1 Kinds of phase transitions

Although phase transitions are classified as first order and second order, there are numerous cases exhibiting features of both [36]. Moreover, there are other criteria too for classification of phase transitions. The main classifications are as follows :

a) Reversible and irreversible phase transitions :

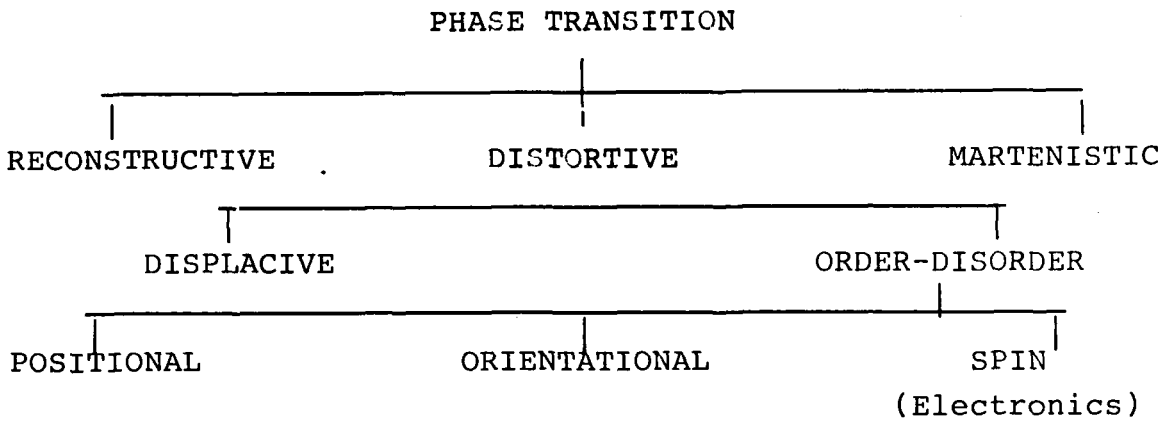
A phase transition in which the system returns to its original phase after removal of the agency or parameter which caused the phase transition is termed as reversible phase transitions. On the other hand if the system does not return to its original phase, then the transition is called irreversible phase transition. The change of graphite to diamond is an example of irreversible phase transition.

b) First order and second order phase transitions :

A first order transition involves a sharp and discrete change in internal and free energies at the transition point. So the system shows a discontinuity in almost all physical and chemical properties (order parameter ψ) at the transition temperature whereas if the transition occurs continuously (that is, $\psi \rightarrow 0$ smoothly) then the transition is said to be second order. Experimentally one can only determine a phase transition to be "nearly second order" since it is always possible for a small jump in ψ or other properties to go undetected. This will be understand whenever we use the term "second order". Near a second order phase transition, the crystal becomes "soft" with respect to the order parameter [44]. During a second order phase transition, the entropy and volume of the system remain continuous while the heat capacity and thermal expansion undergo a discontinuous change [45]. The λ transition is a particular case of second order transition in which the heat capacity tends towards infinity [36].

c) The Bürger classifications :

Different kinds of phase transitions in solids can be categorized into three types following Bürger's classifications [46].



1.8.2 **Reconstructive phase Transitions**

The transitions involve the disruption of old structure and the atoms or molecules of the solid reconstruct a new lattice. These transitions are often slow due to involvement of transport of matter. These transitions are of first order [44]. The modification of a compound from amorphous to crystalline state comes into this category.

1.8.3 **Distortive Phase Transitions**

In a distortive phase transition the linkages at the net are not disrupted but the regular lattice is distorted slightly. This can occur in two different ways :

(i) By small displacements in the lattice positions of single atoms or molecular units known as displacive phase transitions.

ii) May involve changes in the ordering of atoms in various equivalent positions known as order-disorder transitions. Accordingly, the distortive phase transition is called a displacive or order-disorder type. The various equivalent positions in the case of an order-disorder transition may refer to positions of atoms in the lattice or to angular orientations of molecules or ions or to spin of electrons or protons. Accordingly the order-disorder transition is called positional, orientational or spin (electronic/nuclear) order-disorder type. Positional disorder has been observed in various inorganic compounds such as AgI, $RbAg_4I_5$ and orientational disorder has been observed in KCN $NaNo_2$ etc.

The displacive and order-disorder limits can be distinguished interms of a single-cell potential as shown in figure 1.1 [47] for one spatial coordinate Q with an anharmonic potential of the form

$$V(Q) = aQ^2 + bQ^4 \qquad \ldots. \quad (1.26)$$

with constants a <0 and b>0. Equation (1.26), corresponds to a double well potential in which the height of the hump between the two minima is given by $\Delta E = \frac{a^2}{nb}$. when $\Delta E >> KT_c$ the transition occurs due to ordering between $Q_o + \sqrt{\frac{-a}{2b}}$ and $Q_o - \sqrt{\frac{-a}{2b}}$. On the other hand, if we have $\Delta E << KT_c$ a continuous cooperative displacement of atoms

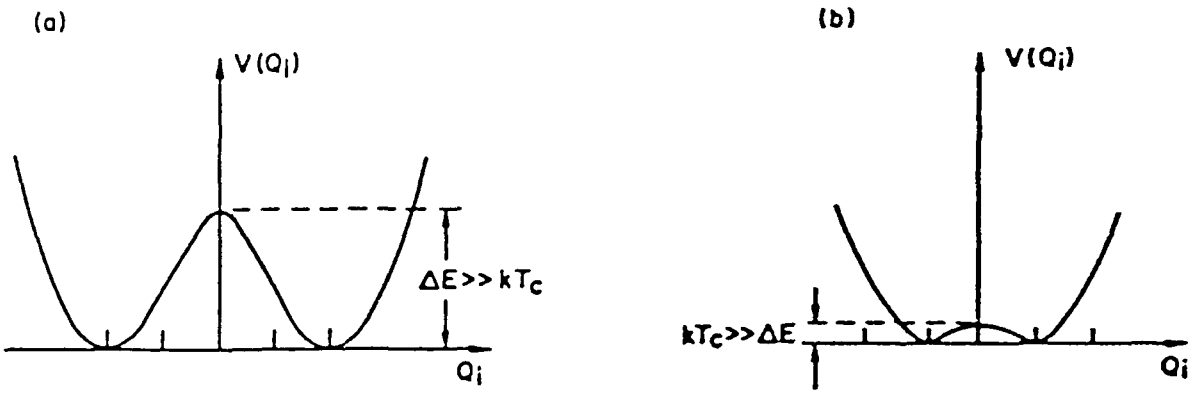


Fig. 1.1. Single cell potentials in (a) order-disorder (b) displacive SPT system

along Q occurs with decreasing temperature. This describes the limiting case of a displacive type of structural phase transition.

1.8.4 Martenistic Phase Transitions

Martenistic phase transitions are polymorphic transitions. In this type of transitions atoms of the crystal lattice do not interchange places [35]. It is a diffusionless transition in which the two phases are related by shear deformations. The transformation usually proceeds by means of the nucleation of new phase crystals inside the initial phase [48].

1.8.5 Incommensurate - commensurate Phase Transitions

Apart from the transitions discussed above a totally different kind of phase transition is known to occur in solids, called incommensurate phase transition. The recent discovery of incommensurately distorted structure has important implications for the study of structural phase transitions [49]. In a few years numerous examples have become known of compounds having in certain temperature interval a structure without any space group symmetry, whereas outside that interval the structure is crystalline. The non-crystalline structure is not amorphous but is well

ordered and may be described as a periodic distortion not filling with the crystal periodicity. The study of the behaviour of incommensurate phase is now a subject of utmost interest theoretically as well as experimentally.

A schematic illustration of the distortion accompanying an incommensurate transition appears in figure 1.2 [50]. In this transition the wave vector associated with order parameter, $\bar{q}_\psi$ is not an integral multiple of a transition vector of the high temperature phase [51]. The eigen Vector of the soft mode $\delta\bar{u}$ corresponds to a two component order parameter depending upon both amplitude and the phase of vector

$$\delta u(r) = \delta u \exp(i\bar{q}_i \cdot \bar{r}) \qquad (1.27)$$

For an incommensurate transition

$$q_i = [2\pi(1-\delta)/na] \qquad (1.28)$$

where a is lattice constant in the high temperature. Phase, n is an integer and δ is an irrational number, small compared to unity. The long wavelength fluctuation about the new structure describing the excitations in the incommensurate phase can be decomposed into two components known as amplitudon and phason. Amplitudon is the amplitude mode, in which the amplitude $|\delta u|$ is uniformally changed and in phason, the phase of the $\delta\vec{u}$ is uniformally shifted

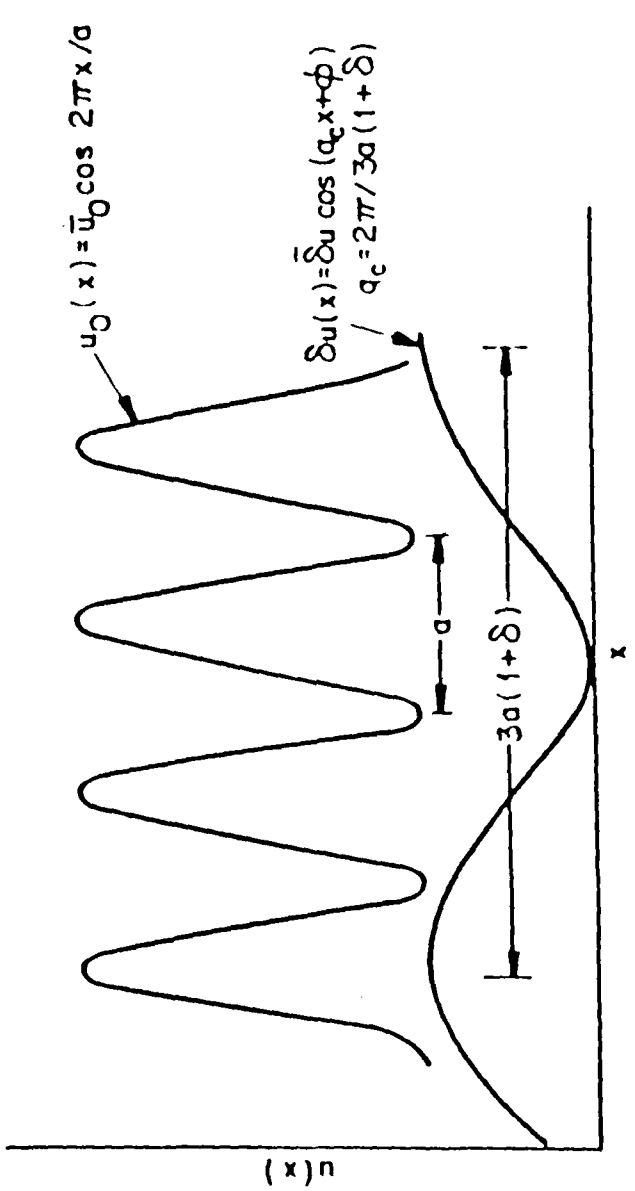


Fig. 1.2 Schematic representation of an incommensurate phase transition. The static particle displacements in the parent phase (u_0) are shown, together with the incommensurate distortion δu. The incommensurate structure is determined by the sum $u_0(x) + \delta u(x)$

$[\partial\vec{u} \longrightarrow \partial u \exp(iQ)$. The amplitude mode behaves as a normal soft mode in the ordered phase of a commensurate transition. The phase mode behaves differently. Because an incommensurate distortion can be uniformally displaced by an arbitrary amount without cost in energy, the frequency of the q = 0 phason must be zero.

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CHAPTER - II

EXPERIMENTAL TEACHNIQUES

2.1 EXPERIMENTAL

This capter briefly describes the techniques used for the preparation of samples under study, their structure confirmation and the measurement of Raman and infrared spectra at room temperature and above.

2.2 PREPARATION AND GROWTH OF CRYSTALS

Single crystals of methylammonium mercury chloride were prepared by slow evaporation of a 1:1 mixture of alcohol and acetone (Tri Distilled) containing a stoichiometric ratio of CH_3NH_3Cl (AR grade, sigma, USA) and $HgCl_2$ (AR grade, SD Fine Pvt, INDIA) [1] at room temperature.

Later, these crystals were redissolved in 1:1 mixture of alcohol and acetoneand large transparent crystals of few mm^3 were obtained by slow evaporation. A good transparent, Polished single crystal was selected for Raman measurements.

2.3 RAMAN SPECTRA

The Raman data were recorded with a Spex model 1403 Ramalog Spectrometer, using a 5 watt Spectra Physics model 165-09 Argon ion laser as exciting source. A block diagram of the experimental set up is shown in Fig. 2.1. To obtain stabilized three phase 203 volts for the laser power supply the three phase mains voltage is first stabilized to 400

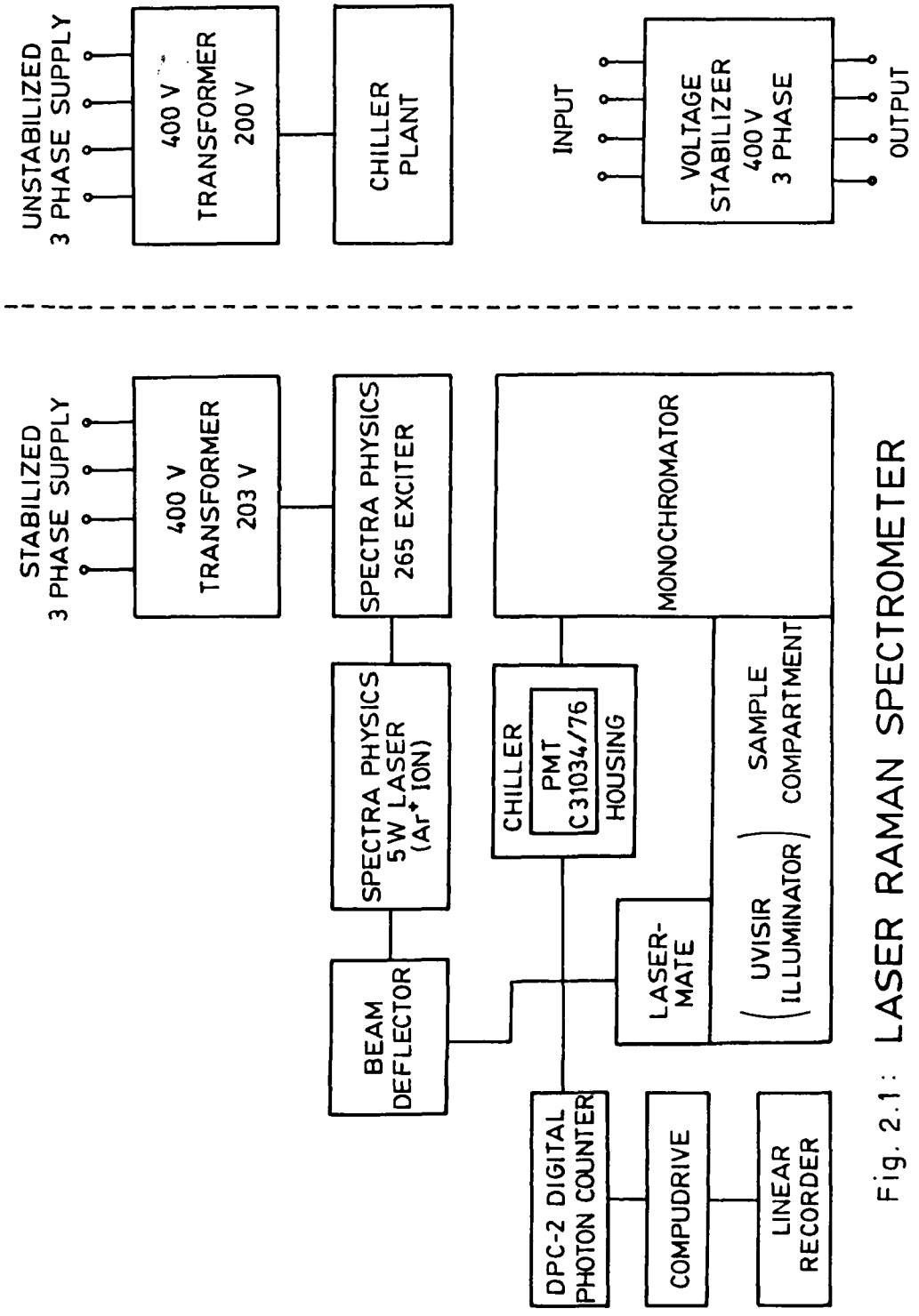


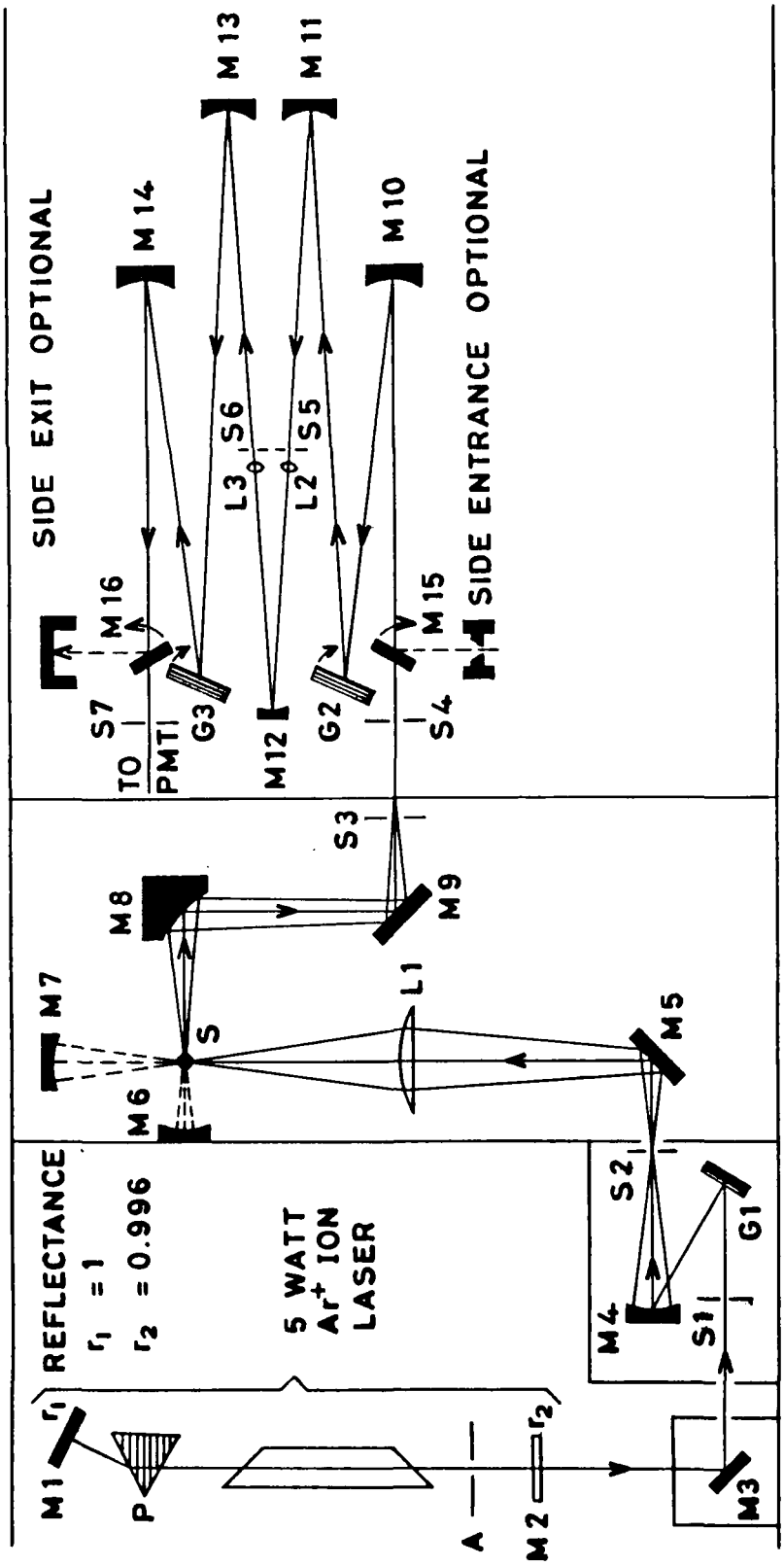
Fig. 2.1: LASER RAMAN SPECTROMETER
(BLOCK DIAGRAM)

volts by a 20 KVA voltage stabilizer and then converted to 203 volts by a 12.0 KVA power transformer. The laser head and its power supply are cooled by distilled water circulated in a closed loop and maintained at a temperature of 20°C by the HX-500 Chilling Plant obtained from Neslab. The heat of the Chilling Plant is dissipated by tap water.

2.3.1 Spex Ramalog 1403 Double Monochromator

The optical diagram of the set up for Raman studies is shown in Fig. 2.2. The Raman spectra were recorded by passing the 514.5 nm laser beam in the light control mode for excitation of the samples. The laser beam passes through the leasermate which filters out the plasma lines. Then it enters the UVISIR illuminator, where a small focal length fused silica condensing lens is used to focus the beam of 1.5 mm diameter to a spot of 10 μm diameter on the sample. The scattered beam is collected by an elliptical mirror and focussed on to the entrance slit of the monochromator. The outcoming radiation falls into a thermo-electrically cooled C-31034 photomultiplier tube (PMT) used as detector. It was cooled to -20°C by a thermoelectric cooling device to reduce the dark currents which arise mainly because of thermionic emission from the photocathode.

The signal is analysed by the Spex photon couting system DPC-2. The DPC-2-signal processing circuit is



P:Prism; A:Aperture; M1-M3, M5, M9, M15, M16:Plane Mirrors; M4, M6, M7, M10-M14:Concave Mirrors; M8:Elliptical Collector Mirror; S1-S7:Slits; G1-G3:Gratings; L1: Fused Silica Condenser Lens; S: Sample; L2, L3: Optical Filter; PMT: Photomultiplier Tube.

FIG.2.2: OPTICAL DIAGRAM OF SPECTRA PHYSICS LASER AND RAMALOG 1403 SPECTROMETER

completely digital. Normally DPC-2 receives analoge signals in the form of DC current. These enter the electrometer module and converted into voltage. This voltage is routed to a V-F (Voltage to frequency converter) and enter the digital signal processing moldules and finally the spectrum is recorded on a linear chart recorder. To study the polarization of Raman bands a polarizer(analyser) is placed before the elliptical mirror and a scrambler is placed before the entrance slit which converts the plane polarized light to circularly polarized light. The plane of polarization of the laser beam can be rotated by 90°, keeping a polarization rotator before the lasermate.

2.3.2 Spectra at room temperature

A good transparent and properly polished single crystal of 5 x 4 x 2 mm^3 was selected for Raman measurements. The sample was illuminated with 514.5 nm line from an Ar^+ laser and the Raman spectra were recorded using a Spex 1403 Ramalog monochromator in random orientation. We could not take the polarization data as the crystal morphology is not known.

2.3.3 Spectra at high temperature

The Raman spectra at high temperature were recorded with a locally fabricated cell as shown in Fig. 2.3. It

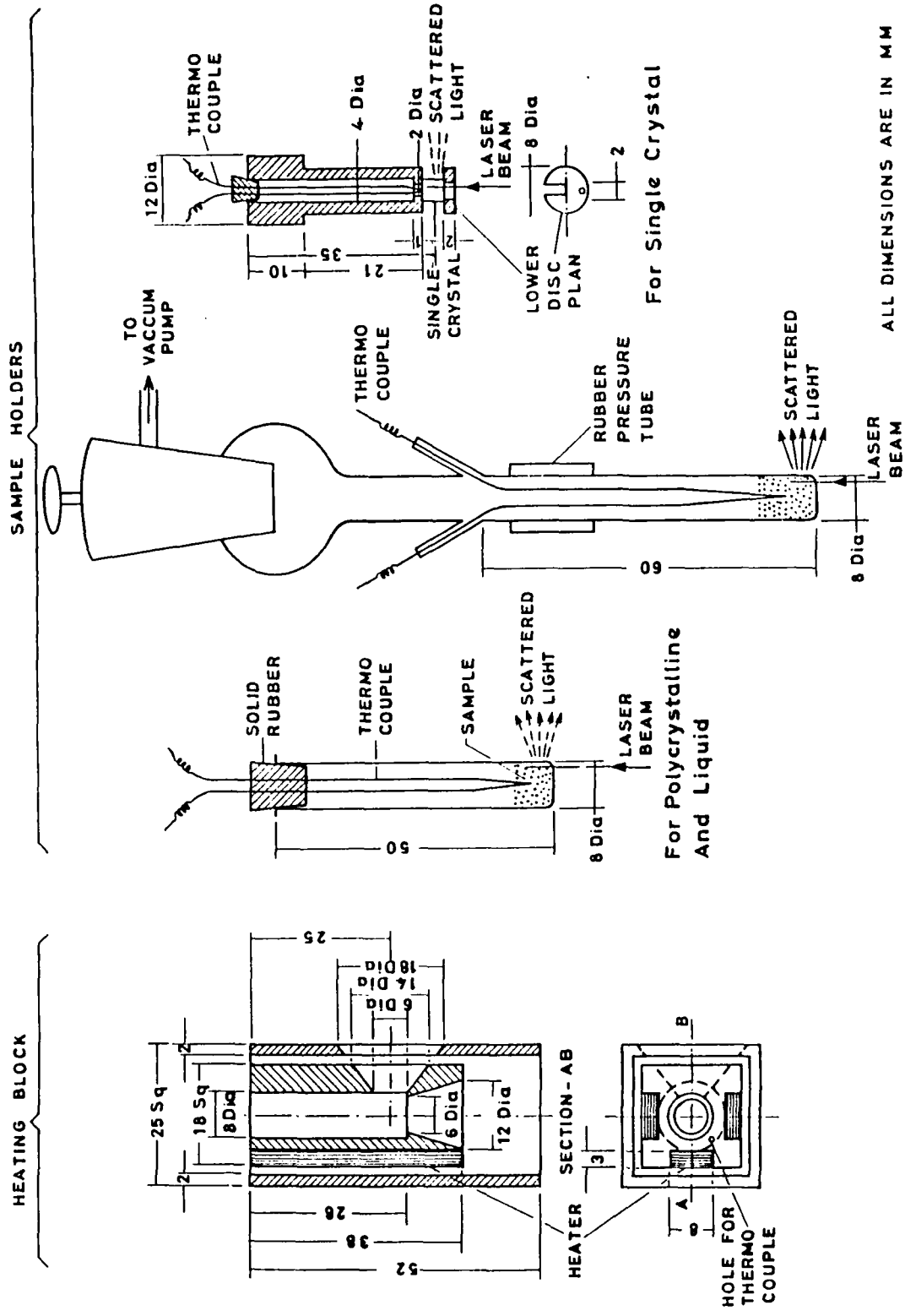


Fig. 2.3 : The design of a high temperature cell with diffenent types of sample holders for Raman Studies

consists of three parts : (i) The heating block (ii) The sample holder and (iii) The temperature controller.

The heating block (18 x 18 x 38 mm^3) with a 8 mm diameter hole drilled to a depth of 28 mm (to insert the sample holder) is made of brass. This is heated from three sides by 25 watts heater fitted into properly created grooves. On the bottom and the fourth side two conical holes are drilled to admit the exciting radiation and collect the scattered radiation, respectively. The whole system is mounted on a Spex three way motion platform to permit alignment of the sample.

The crystal was kept in this temperature cell holder. A Specac temperature controller with copper-constantan thermocouple was kept in close contact with the sample to measure the sample temperature with an accuracy of $\pm$1K. We also used 514.5 nm line from Ar^+ laser and Spectra were recorded in randon orientation by Spex 1403 Ramalog monochromator.

2.4 THE IR INSTRUMENT

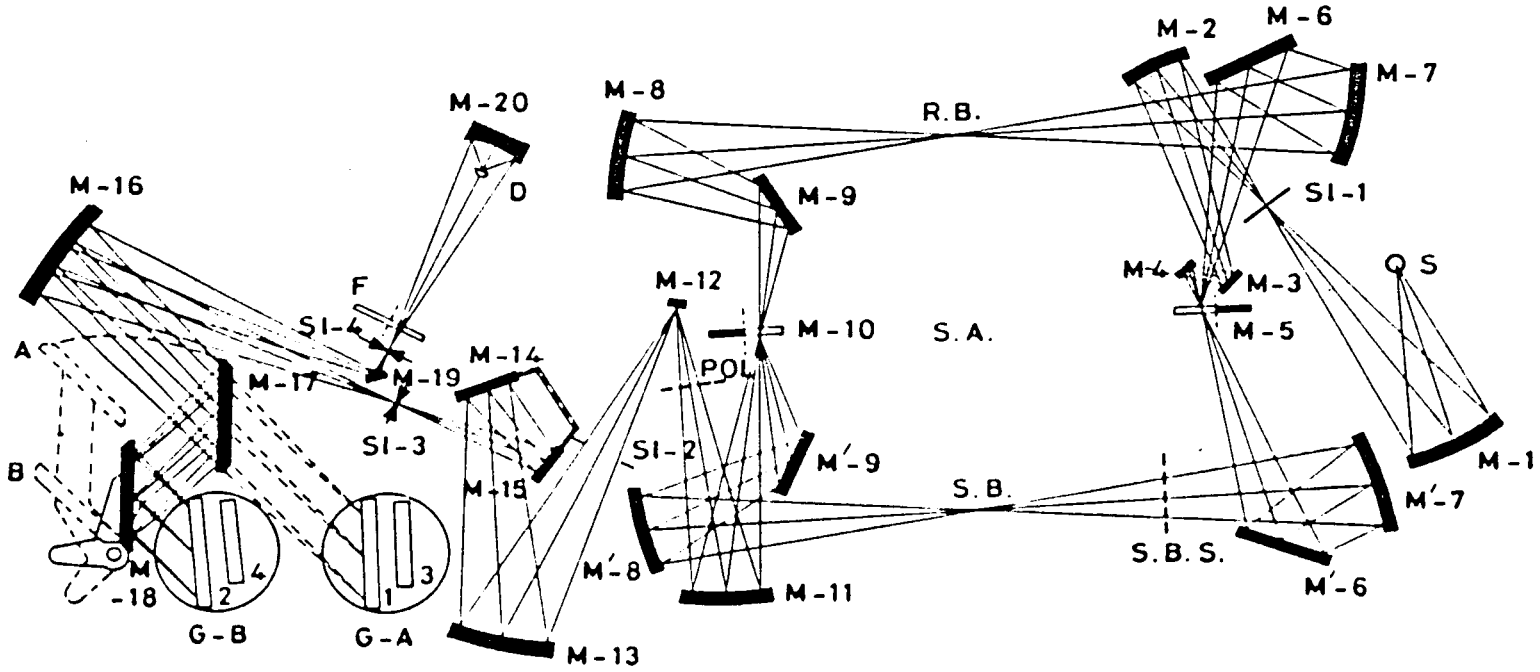
The concept of automatic percent transmission recording using the optical mull principle for IR spectrometers was introduced in 1942 and several successful systems were developed [2]. All of them have in common a double

path of source illuminating the monochromator entrance slit with a rotating mirror means of flickering alternately between the reference and sample path. The detector responds only when the intensity of the two beams is unequal. The recording system responds to any unbalance by causing a light attenuator to move in or out of the reference beam to restore balance. The recording pen is coupled to the light attenuator so that it records the attenuator position as an indication of sample percent transmission. The infrared transmission spectra at room temperature in the FIR region were performed with a commercial Perkin Elmer 580 spectrometer with dry air purging system. Its details are well described elsewhere [3]. The optical diagram is shown in Fig. 2.4. The spectrum of the polystyrene was used for callibration of the frequency scale.

2.5 SCAN OF THE IR SPECTRA

The transmission spectra at room temperature in NIR spectral regions were recorded on powdered (microcrystalline) samples on KBr pellets and Nujol mull. For obtaining good transmission spectra extemely thin samples (0.1 μ) are needed because of the high absorption associated with fundamental lattice modes. However, the IR study of the single crystals can be made either by specular

FIG.2.4: OPTICAL DIAGRAM OF PERKIN-ELMER MODEL 580 INFRARED SPECTROPHOTOMETER



S:Source; M1, M2, M4, M7, M'7, M8, M'8, M11-M13: Toroid Mirrors; M5, M10: Chopper Mirrors; M3, M6, M'6, M9, M'9, M14, M15, M17, M19: Reflection and Scatter Grating Surface Mirrors; M16: Paraboloid Mirror; M20: Elipsoid Mirror; G-A, G-B: Grating Tables; SI-1: Baffle and Secondary Source; SI-2: Pupil Baffle; SI-3: Entrance Slit; SI-4: Exit Slit, POL: Polarizer Accessory; F: Optical Filter; D: Detector; SBS: Sample Beam Shutter; SB: Sample Beam; SA: Sample Area; RB: Reference Beam.

reflectance or by attenuated total reflection-techniques [3,4,5]. Generally pressed disc [6] and nujol mull techniques [7,8] are used to study the transmission spectra in powder form. It is required for both the techniques that the particle size of the solid should ideally be less than the wavelength of the incident radiation because this brings down the probability of the phenomena of reflection and refraction that might show their serious effect on the recorded speectra. Moreover, the same condition minimizes the scattering as well as Christionsen effect that are generally present in the spectra. Now we discuss these techniques in some detail.

2.5.1 **The mull technique**

This technique is accomplished by grinding the solid in a mineral oil generally - Nujol, to make a thin paste. The mineral oil serves to suspend the solid and act as a coating around the particles so as to match the refractive indices of the solid and mineral oil more closely than done by air. When the cream like suspension is uniform, it is squeezed into a thin layer between well polished NaCl, KBr pelletes and mounted in the sampling area of the spectro-photometer. Another demountable cell between the pellets of which a few drops of Nujol are placed, is kept in the reference beam to compensate for the absorption

bands of Nujol.

Since Nujol absorbs at 2915,1462,1376 and 719 cm^{-1} one can not draw fruitful information about the samples having absorption around these frequencies [9]. Therefore, other mulling agents such as Fluorolube or hexachlorobutadiene (HCBD) have been suggested as none of these liquds absorbs in the region where Nujol does.

This technique is used for a qualitative analysis of samples. Since adequate control over sample thickness, dispersion uniformity and paste density can not be maintained, even the use of international standards (such as lead thiocyanate and hexabromobenzene) will not give the satisfactory quantitative analysis from mulls.

2.5.2 The Pressed disc (Pellet) technique

This procedure for preparing solid samples for spectral scanning was introduced by Schiedt [6] and Stimson [10]. Their assumption was that a solid can assimilate properly with a suitable matrix material (generally alkali halides) and by applying a pressure of the order of 15000 $lbs/inch^2$ by means of a hydraulic press, a transparent disc can be prepared. The chosen matrix material should have its refractive index comparable to that of the sample and should show high transmittance throughout the spectral range of the instrument alongwith its stability and non-hygroscopi-

city. The matrix materials generally used are the alkali halides : KBr, KCl, NaCl, KI and Cs Br etc. Among these KBr is most widely used.

In order to obtain a good spectrum, attempts were made to keep the particle size smaller than the wavelength of the incident radiation with the use of an agate motar and pestle.

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CHAPTER - III

VIBRATIONAL SPECTRA AND PHASE TRANSITION

VIBRATIONAL SPECTRA AND PHASE TRANSITION

3.1 INTRODUCTION

Methylammonium mercury chloride ($CH_3NH_3HgCl_3$) is an interesting solid because it undergoes [1-4] a rather peculiar ferroelectric phase transition at Tc = 60°C. Instead of decreasing, the point group symmetry increases on going from the paraelectric to the ferroelectric phase. The high temperature paralectric phase is monoclinic with space group C_2 and in the ferroelectric phase below Tc the space group is trigonal, $P3_2$. Earlier work on this crystal includes X ray diffraction studies [4], Cl^{35} NQR studies of the structural phase transitions [2], proton^{14}-N double resonence studies of the ferroelectric phase transitions [5], dielectric studies by differential scanning calorimetry [6] and microwave anisotropy and dichroism by a resonant cavity method [7]. $CH_3NH_3HgCl_3$ belongs to perovskite - type ABX_3 compounds and consists of $CH_3NH_3^+$ and $HgCl_3^-$ ions. The role of these molecular vibrations can be effectively studied by IR and Raman spectroscopy. IR and Raman studies have yet not been done in this system. We have recorded the Raman spectra in random orientation of the crystal at room temperature to study the normal modes of vibrations. Polarisation measurements in the crystal could not be

recorded since the crystal morphology is not known. The absorption spectra in the NIR regions at room temperature have been recorded to facilitate the identification of the vibrational modes.

The $CH_3NH_3^+$ groups play an important role in phase transition mechanism [5]. That is why we have selected a particular thermosensitive $CH_3NH_3^+$ stretching mode in order to throw some light on the role of these groups in the phase transition mechanism and confirm the transition known to occur around 60°C.

3.2 CRYSTAL STRUCTURE

At room temperature Methylammonium mercury chloride crystallizes in a trigonal structure having three molecules per unit cell (z = 3). The space group is trigonal $P3_2(C_3^3)$ with a = b = 7.817 Å, c = 9.826 Å, β = 90° and γ = 120°. In the high temperature paraelectric phase the space group is monoclinic $C_2(C_2^3)$ with a = 13.816 Å, b = 7.880 Å, c = 9.734 A, β = 90.49° with six formula units per unit cell (z = 6) [1-4].

The Hg atom in $CH_3NH_3HgCl_3$ is involved in two short Hg-Cl bonds and two long Hg-Cl bonds. A fifth Hg-Cl contact is found but it is doubtful. The bonding between methylammonium and the mercury chloride groups is expected

to result from N-H...Cl hydrogen bonds. Each NH_3 unit is coordinated by five Cl atoms at distances suitable for H-bond formation. Consequently it is not possible to predict which atoms are involved in hydrogen bonds. The methylammonium groups can be rotationally distorted about the C-N axis, to include all five Cl atoms in the hydrogen bonding scheme [1]. The view of the crystal structure is shown in Fig. 3.1.

3.3 GROUP THEORETICAL ANALYSIS

The factor group C_3 has two symmetry species A and E. Vibrations belonging to species A and E show both Raman and infrared activity. The vibrations of A type symmetry are allowed in XX + YY and ZZ polarization geometries and those of E symmetry are allowed in (XX - YY, XY) and (XZ, YZ).

We have classified normal modes of the crystal using correlation method after Fately et al. [8]. For correlation method, the site symmetry of each equivalent set of atoms or ions should be known. In the present crystal there are two equivalent sets of ions. They are three $CH_3NH_3^+$ ions and three $HgCl_3^-$ ions. Both the sets, each of three equivalent ions, will be at different C_1 sites since only C_1 site of multiplicity is present. The group theory predicts 108 vibrational species including 3 acoustic modes. The total

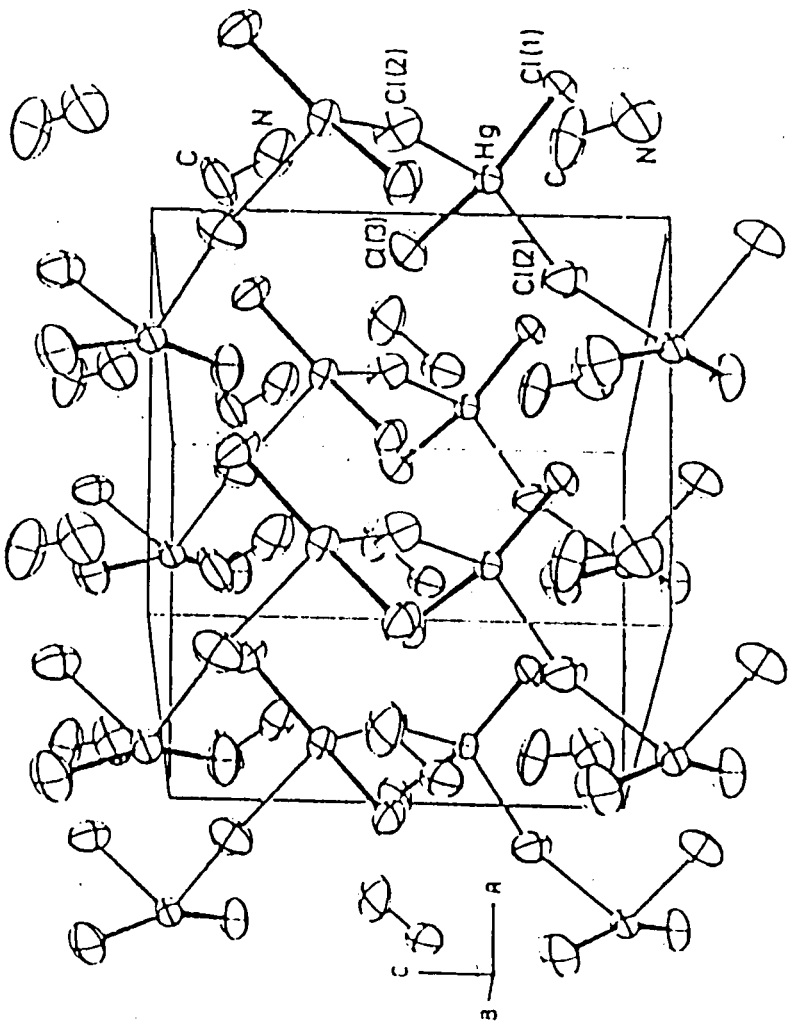

Fig. 3.1 View of the crystal structure of $CH_3NH_3HgCl_3$

108 phonon modes have been grouped into 54 internal modes of $CH_3NH_3^+$ ions, 18 internal modes of $HgCl_3^-$ ions and 36 external modes of the crystals.

The correlation between different symmetry species of free state point groups, site symmetry point groups and the crystal factor group in ferroelectric phase (below Tc) is given in Table 3.1. Using these correlations of the symmetry species, the number of phonon modes arising from a definite mode of free state $CH_3NH_3^+$ and $HgCl_3^-$ ions alongwith libratory and translatory modes have been given in Table 3.2.

3.4 RESULTS AND DISCUSSION

3.4.1 Vibrational spectra and assignment at room temperature

The Raman spectra (15-3215 cm^{-1}) of the crystal have been measured at room temperature and above Tc in random orientation and infrared absorption spectra (200-4000 cm^{-1}) have also been recorded at room temperature. The Raman spectrum forms the basis of the vibrational assignments. In view of this fact the identification of observed bands has been discussed interms of their frequencies in Raman spectra. The Raman spectra and IR spectra of the crystal

Table 3.1 Correlation between different species of C_{3v}, D_{3h}, C_1 and C_3 point groups (phase II) below Tc.

Structural group	Symmetry Species		
	Free state	Site group	Crystal factor Group
$HgCl_3^-$	$\underline{D_{3h}}$	$\underline{C_1}$	$\underline{C_3}$
	A_1'	A	(A+E)
	A_2''	A	(A+E)
	E"	2A	2(A+E)
	E"	2A	2(A+E)
$CH_3NH_3^+$	$\underline{C_{3v}}$	$\underline{C_1}$	$\underline{C_3}$
	A_1	A	(A+E)
	A_2	A	(A+E)
	E	2A	2(A+E)

Table 3.2 Classification of phonons in $CH_3NH_3HgCl_3$ crystal (Phase II) below Tc (site symmetry approach).

Modes	Species under C_3^3		N^a
	A	E	
I. Internal modes of $HgCl_3^-$ (D_{3h}) : Site C_1			
$\nu_1(A_1)$	1	1	3
$\nu_2(A_2)$	1	1	3
$\nu_3(E")$	2	2	6
$\nu_4(E")$	2	2	6
Total internal modes of $HgCl_3^-$:	6	12	18
II. Internal modes of $CH_3NH_3^+$ (C_{3v}) : Site C_1			
$\nu_1(A_1)$	1	1	3
$\nu_2(A_1)$	1	1	3
$\nu_3(A_1)$	1	1	3
$\nu_4(A_1)$	1	1	3
$\nu_5(A_1)$	1	1	3
$\nu_6(A_2)$	1	1	3
$\nu_7(E)$	2	2	6
$\nu_8(E)$	2	2	6
$\nu_9(E)$	2	2	6
$\nu_{10}(E)$	2	2	6
$\nu_{11}(E)$	2	2	6
$\nu_{12}(E)$	2	2	6
Total internal modes of $CH_3NH_3^+$:	18	36	54

Contd....

Contd....(Table 3.2)

III. External modes

(a) Translatory modes of $HgCl_3^-$	3	3	9
(b) Libratory modes of $HgCl_3^-$	3	3	9
(c) Translatory modes of $CH_3NH_3^+$	3	3	9
(d) Libratory modes of $CH_3NH_3^+$	3	3	9
Total external modes :	12	24	36
Grand total :	36	72	108

N^a - Total phonon modes originating from a particular mode of vibration.

are shown in Fig. 3.2 and 3.3. The vibrational modes of the crystal are identified in terms of internal modes of $CH_3NH_3^+$ and $HgCl_3^-$ ions and lattice modes.

3.4.2 Internal modes of $CH_3NH_3^+$ ions

The free ion $CH_3NH_3^+$ posseses C_{3v} symmetry. There are twelve fundamental internal modes of vibration of $CH_3NH_3^+$ ions. Five ($\nu_1 - \nu_5$) of them are totally symmetric A_1 type, one (ν_6) asymmetric A_2 type non-degenerate, and the rest six ($\nu_7 - \nu_{12}$) are doubly degenerate E type vibrations. The vibrations of A_1 and E species are Raman and IR active whereas A_2 type are IR and Raman inactive. The assignment of the vibrational modes has been made by comparing our spectra with those of Methylammonium chloride [9,10] and Methylammonium metal chloride[11,12].

The strong sharp band at 2976 cm^{-1} is assigned to totally symmetric NH_3 stretching ν_1 mode. The very weak broad bands at 3045 and 3202 cm^{-1} are assigned to CH_3 asymmetric stretching mode ν_8 and asymmetric NH_3 stretching mode ν_7 respectively. Band at around 2900 cm^{-1} is identified with totally symmetric CH_3 stretching mode ν_2. The band around 1487 cm^{-1} is assigned to ν_{10} asymmetric CH_3 bending and very weak band observed around 1426 cm^{-1} is assigned to ν_4 symmetric CH_3 bending modes. A very weak

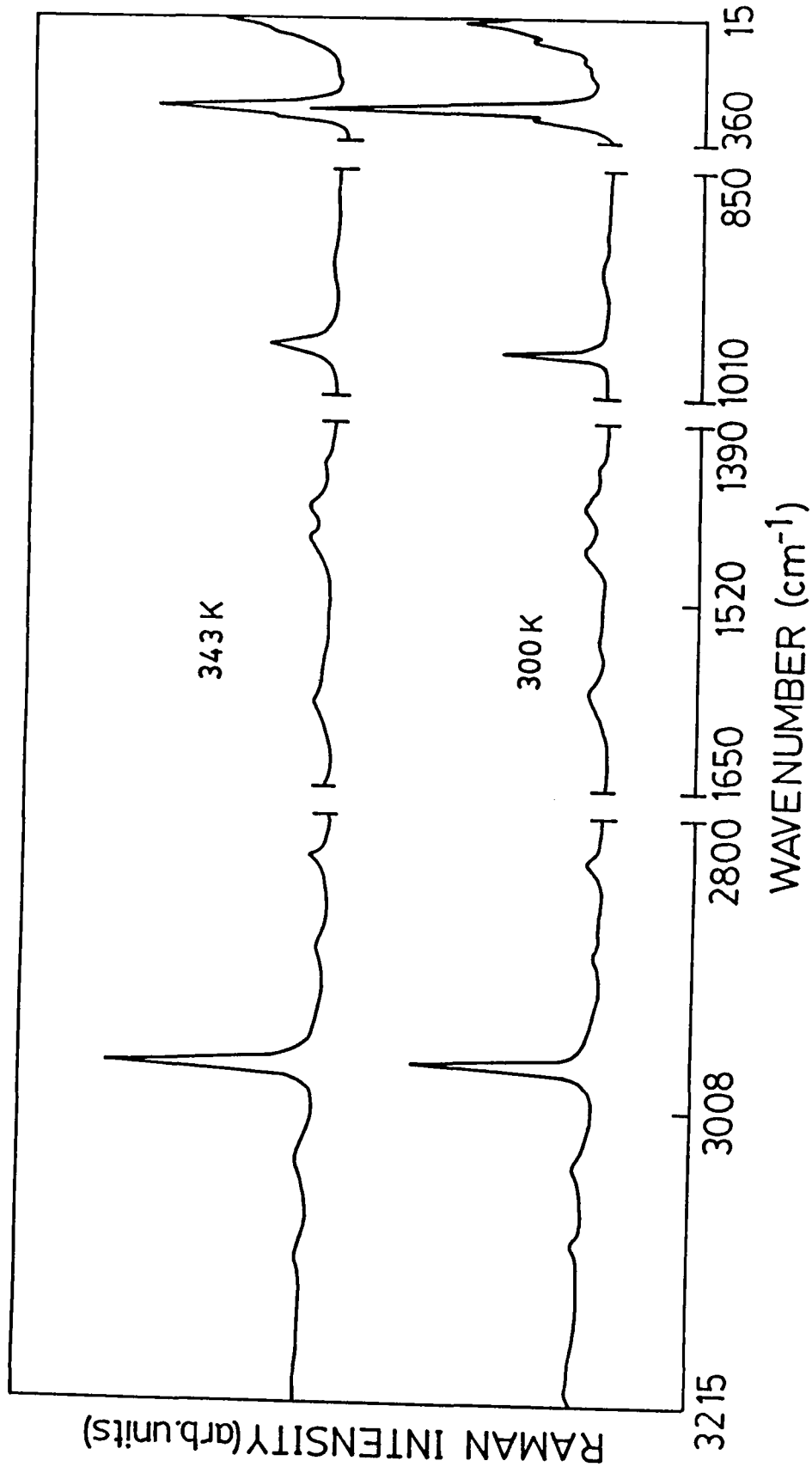

FIG.3.2: UNPOLARIZED RAMAN SPECTRA OF $CH_3NH_3HgCl_3$ AT ROOM TEMPERATURE AND ABOVE TRANSITION TEMPERATURE

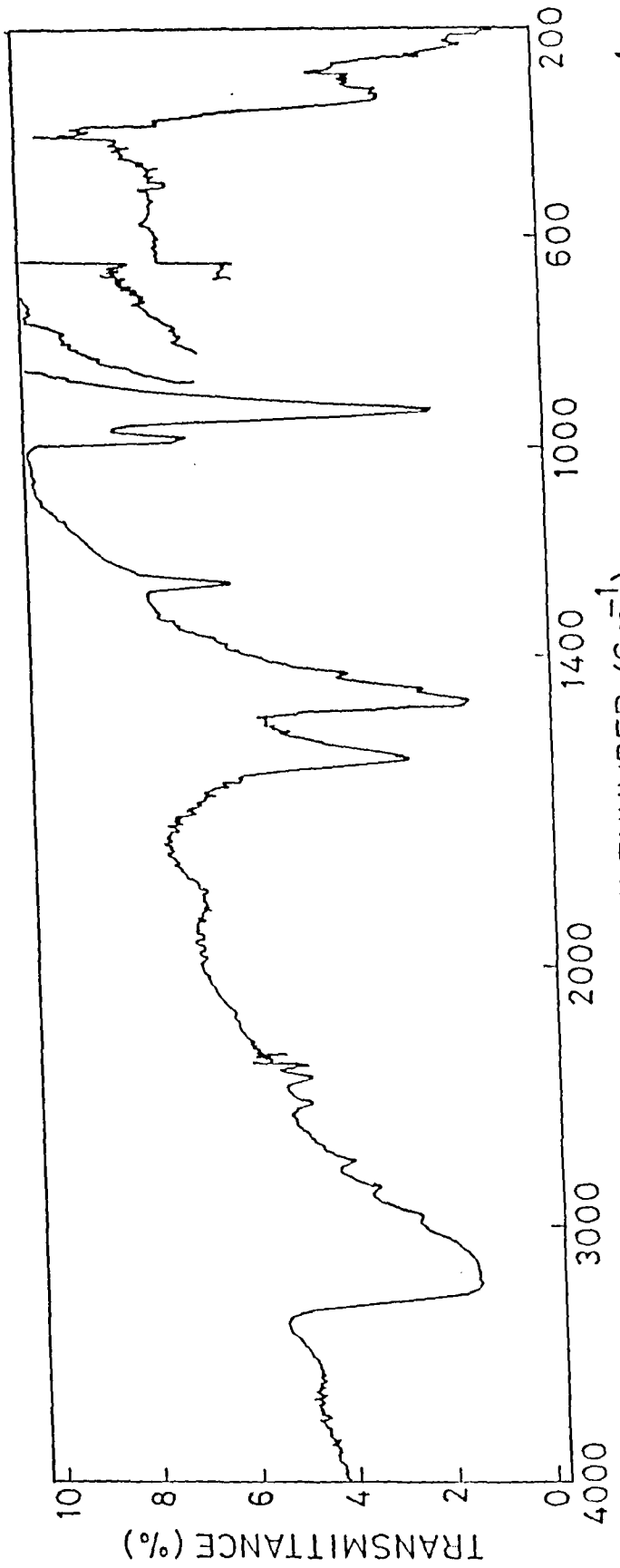

Fig.3.3: Infrared spectra of $CH_3NH_3HgCl_3$ at room temperature (200–4000 Cm^{-1})

broad band at the frequency 1580 cm^{-1} is identified with asymmetric NH_3 bending mode ν_9. A very weak broad band around 1550 cm^{-1} is assigned to symmetric NH_3 bending mode ν_3. The CH_3 rocking mode ν_{12} is observed at 921 cm^{-1}. The rocking mode ν_{11} of NH_3 group is not observed in Raman spectra but in IR it is observed around 1251 cm^{-1}. The strong sharp peak observed at 979 cm^{-1} is identified with C-N stretching mode ν_5. The observed frequencies in IR and Raman spectra with their assignment are given in Table 3.3.

3.4.3 Internal modes of $HgCl_3$ ions

The free $HgCl_3^-$ ion has a planar trigonal configuration with a maximum separation for the three halide atoms predicted. There are four fundamental internal modes of vibration of $HgCl_3^-$ ions. These are denoted as $\nu_1(A')$, $\nu_2(A")$, $\nu_3(E")$ and $\nu_4(E")$ [13]. The internal modes of $HgCl_3^-$ ions have been assigned by comparing our Raman spectrum with those reported for $[Me_3S]$ $[HgCl_3]$ and $HgCl_3^-$ [13-15].

The strong sharp band appearing at 264 cm^{-1} is assigned to symmetric stretching mode ν_1 of $HgCl_3^-$ ion. The broad band at 290 cm^{-1} is assigned to asymmetric stretching mode ν_3. A very weak band at around 116 cm^{-1} is assigned to the bending vibrations of ν_4 $(HgCl_3)$ ions.

Table 3.3 Raman and Infrared frequencies and their assignment at room temperature.

Raman frequency (cm^{-1})	Infrared frequency (cm^{-1})	Assignments
30w		
48vw		
78vw		
116vw		$HgCl_3$ bending mode (ν_4)
166vw		
264vs		Sym. $HgCl_3^-$ stret. mode (ν_1)
290w		Asym. $HgCl_3^-$ stret. mode (ν_3)
921vw	921vs	CH_3 rocking mode (ν_{12})
979m	976m	C-N stret. (ν_5)
	1251m	NH_3 rocking mode (ν_{11})
1426vwb	1426w	Sym. CH_3 bending mode (ν_4)
1457	1456	
1487	1476vs	Asym. CH_3 bending (ν_{10})
1550vvw		Sym. NH_3 bending mode (ν_3)

Contd....

Contd....(Table 3.3)

1584vwb	1588s	Asym. NH_3 bending mode (ν_9)
	1846vvw	
	2156vw	
	2400w	
	2500	$2\nu_{11}$
	2540vw	
	2720w	
2887	2830w	Sym. CH_3 stret. mode (ν_2)
2976s	2960vw	Sym. NH_3 stret. mode (ν_1)
3045vwb	3100vw	Asym. CH_3 stret. mode (ν_8)
3202vwb	3190vs	Asym. NH_3 stret. mode (ν_7)

w - weak; vw - very weak; vvw - very very weak;
m - medium; s - strong; b - broad.

Some bands have been found in the lattice mode region. To identify them unambigously further analysis of FIR and Raman spectra is required.

3.5 PHASE TRANSITION

The phase transition is characterized with the temperature dependence of ν^{C-N} (A_1) stretching mode. This is the most thermosensitive band which we have observed and selected for this study. Fig. 3.4 shows the temperature dependence of C-N stretching mode between 318K to 343K. The frequency versus temperature curve for this band is shown in Fig. 3.5. A plot of full width at half maximum intensity (FWHM) and peak intensity as a function of temperature are displayed in Figs 3.6 and 3.7. The important features of the temperature dependence of Raman spectra of the system are as follows:

(i) The frequency of the band associated with this mode decreases linearly with increasing temperature. Around 330K it showed abrupt discontinuity in the frequency. There is a frequency shift of 5 cm^{-1} for C-N stretching mode (as shown in Fig. 3.4) between 318 to 343K. This shows that there is a change in force constant.

(ii) The full width at half maxima (FWHM) of the band

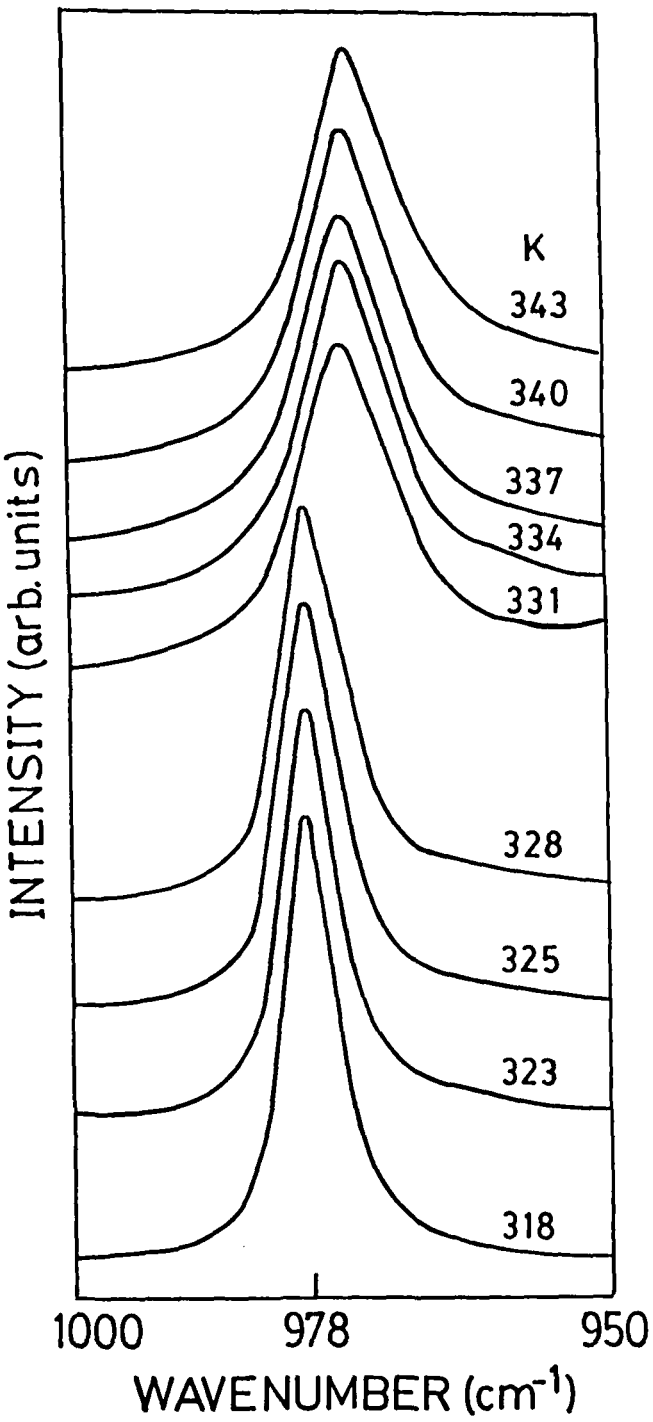

FIG.3.4: TEMPERATURE DEPENDENCE OF RAMAN SPECTRA IN C-N STRETCHING REGION.

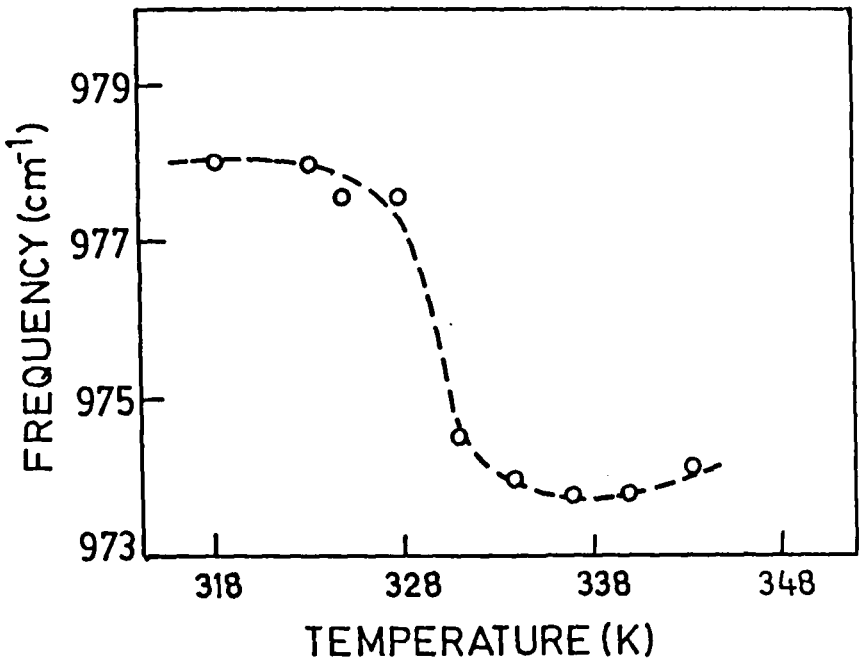

FIG.3.5: VARIATION IN PEAK FREQUENCY WITH TEMPERATURE

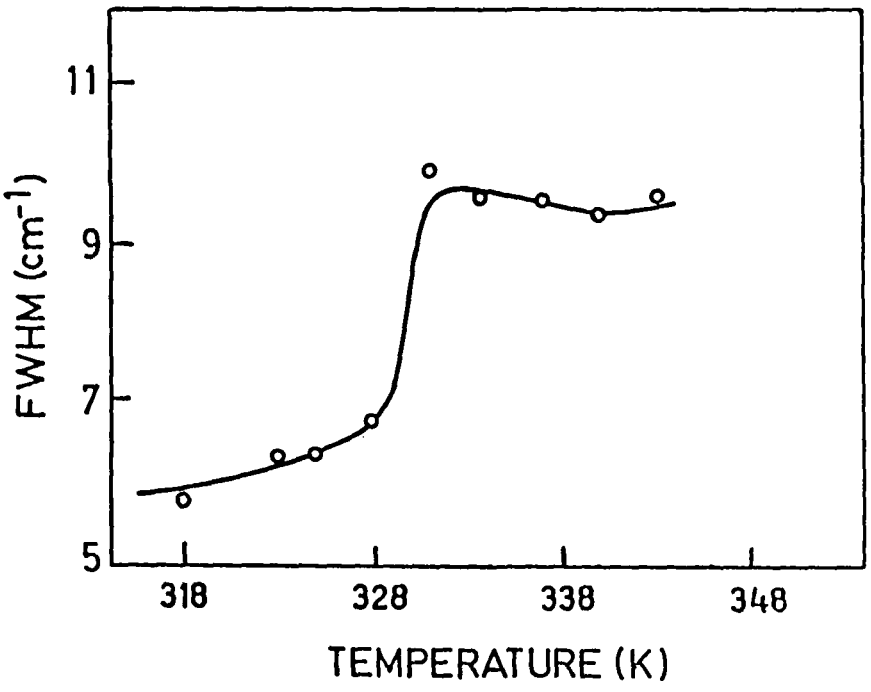

FIG.3.6: CHANGE IN FULL WIDTH AT HALF MAXIMUM INTENSITY (FWHM) WITH TEMPERATURE

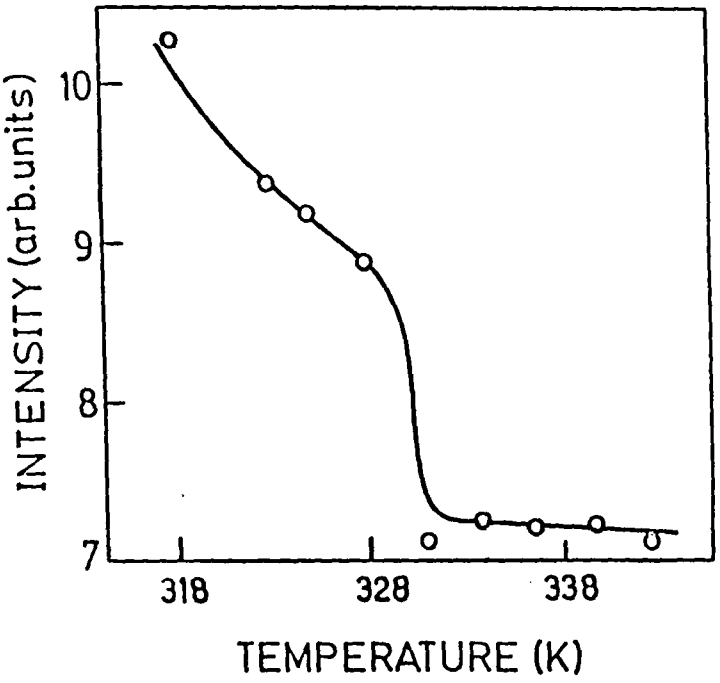

FIG.3.7: VARIATION IN PEAK INTENSITY WITH TEMPERATURE

shows discontinuity at around 330K.

(iii) The intensity decreases continuously in a well defined manner as the temperature increases. But at around 330K a sharp change with discontinuity is observed in the intensity versus temperature curve.

The sharp changes and discontinuities observed in the frequency shift and FWHM alongwith a discontinuous change in intensities with temperature at 330K (57°C) are typical features associated with phase transitions of the first order type.

The band is broad in the higher temperature phase of $CH_3NH_3HgCl_3$ suggesting the presence of appreciable motion of the $CH_3NH_3^+$ group in this phase [11].

CONCLUSIONS

1. The sharp changes and discontinuities observed in the frequency shift and FWHM alongwith intensities as a function of temperature indicate that the phase transition is of the first order type.

2. Broadening of the band in higher temperature phase suggests the presence of appreciable motion of $CH_3NH_3^+$ group.

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